

The Crystal Structure of Bis [benzoato- μ -(2-diethylaminoethanolato- N,μ -O)copper(II)]

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The crystal structure of $\text{Cu}_2 [(\text{C}_2\text{H}_5)_2\text{NC}_2\text{H}_4\text{O}]_2 \cdot (\text{C}_6\text{H}_5\text{COO})_2$, $\text{C}_{26}\text{H}_{38}\text{Cu}_2\text{N}_2\text{O}_6$ is monoclinic with space group $P2_1/c$ and $a=8.721(5)$ Å, $b=8.263(5)$ Å, $c=19.395(7)$ Å and $\beta=100.06(4)^\circ$. The structure was established by Patterson and Fourier methods and refined by least-squares calculations to an R value of 0.056 for 1814 reflections (4240 total).

The structure is dimeric, with two copper(II) ions bridged by 2-diethylaminoethanolato oxygen atoms [$\text{Cu}\cdots\text{Cu}$ 3.011(1) Å]. The coordination of the copper(II) is slightly distorted square-planar. The basal plane consists of one nitrogen atom, two bridge oxygen atoms and one benzoato oxygen atom with bond lengths 2.042(4), 1.902(4), 1.925(4) and 1.888(4) Å, respectively.

The carbon atoms in the 2-diethylaminoethanolato ligand are disordered having the site occupation factors 0.5. The form A is converted into the form B by rotation around the Cu–N bond, 48.0° on the average. The benzoato ligand is unidentate and almost planar.

The structures of many alkoxy-bridged copper(II) complexes with N,N -dialkylaminoethanols ($\text{R}_2\text{NCH}_2\text{CH}_2\text{OH}=\text{R}_2\text{LOH}$) as the second ligand have been reported.¹ Only one benzoate complex is known, the structure of which contains linear trinuclear oxygen-bridged arrays of copper atoms.² Now we have made in the $(\text{C}_2\text{H}_5)_2\text{LOH}$ series the benzoate complex of bis[benzoato- μ -(2-diethylaminoethanolato- N,μ -O)copper(II)].

EXPERIMENTAL

The copper(II) benzoate was made from basic copper(II) carbonate (Merck) and benzoic acid by the method of Bateman and Conrad.³ Of the salt,

0.01 mol was dissolved in methanol and to this solution 0.01 mol of 2-diethylaminoethanol (Fluka AG) was added with stirring. The solution was filtered and precipitation of the compound was achieved by adding some acetone. After some weeks at ambient temperature, dark blue crystals were obtained.

The unit cell parameters and the orientation matrix were determined by a least-squares refinement from 19 centered reflections measured at ambient temperature on a Nicolet R3m diffractometer. Intensity data were collected ($3^\circ < 2\theta < 60^\circ$) in the ω -scan mode, using graphite-monochromatized $\text{MoK}\alpha$ radiation. The scan speed varied from 2.0 to $29.3^\circ/\text{min}$. Two selected reflections were monitored as standards after every 98 measurements. Their intensities showed no significant changes with time. The intensities were corrected for Lorentz and polarisation effects and for absorption from empirical ψ -scan data. Out of 4240 reflections 1814 were retained in subsequent calculations, using an acceptance criterion of $F_o > 5\sigma(F_o)$.

CRYSTAL DATA

$\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})(\text{C}_7\text{H}_5\text{O}_2)$, $FW=300.85$
 Space group: $P2_1/c$ (No. 14)
 $a=8.721(5)$, $b=8.263(5)$, $c=19.395(7)$ Å
 $\beta=100.06(4)^\circ$
 $V=1376.19$ Å³, $Z=4$, $F(000)=628$
 $\mu(\text{MoK}\alpha)=16.5$ cm⁻¹, $\lambda(\text{MoK}\alpha)=0.71069$ Å
 $D_m=1.44$ g cm⁻³ (floatation technique)
 $D_x=1.45$ g cm⁻³

STRUCTURE DETERMINATION

The positional parameters of the copper atom were obtained from the sharpened Patterson map. The remaining non-hydrogen atoms of the structure were found from successive Fourier syntheses. The

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) for non-hydrogen atoms with e.s.d. in parentheses. The occupancy factors of A and B positions of carbon atoms are 0.5.

Atom	X	Y	Z	U^a	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu	-222(1)	1259(1)	535(1)	34(1)	31(1)	41(1)	-5(1)	5(1)	-3(1)
O1	-978(4)	-795(5)	185(2)	39(2)	41(2)	58(3)	-14(2)	17(2)	-14(2)
O2	587(5)	3320(4)	819(2)	45(2)	35(2)	63(3)	-13(2)	-1(2)	-4(2)
O3	2779(6)	2166(5)	1346(3)	76(3)	30(2)	83(4)	0(2)	-13(3)	6(2)
N	-1992(5)	1158(5)	1097(2)	57(3)	54(3)	63(3)	-11(3)	27(3)	-13(3)
C1A	-2228(8)	-1486(13)	460(5)	41(3)					
C1B	-2516(6)	-1194(9)	262(5)	50(3)					
C2A	-2316(28)	-639(14)	1123(9)	114(18)	98(16)	135(19)	-61(14)	96(16)	-72(14)
C2B	-3162(14)	-36(24)	718(13)	62(13)	89(14)	191(25)	-72(17)	72(14)	-23(11)
C3A	-3341(15)	2166(20)	721(11)	48(10)	103(15)	156(21)	-33(16)	53(12)	-7(10)
C3B	-2799(27)	2707(19)	1259(10)	122(18)	94(15)	109(17)	-21(13)	72(15)	45(13)
C4A	-2987(26)	4030(19)	712(11)	80(7)					
C4B	-3228(23)	3657(23)	550(9)	61(5)					
C5A	-1424(21)	1693(20)	1872(7)	152(19)	83(14)	81(13)	-43(11)	90(14)	-31(13)
C5B	-1625(22)	178(21)	1794(8)	118(17)	82(13)	82(13)	27(11)	37(12)	-2(12)
C6A	155(23)	992(36)	2217(12)	102(10)					
C6B	-265(20)	1000(26)	2277(9)	56(5)					
C7	2006(7)	3347(6)	1162(3)	54(4)	29(3)	44(3)	-7(3)	7(3)	-4(3)
C8	2650(7)	5036(7)	1331(3)	46(3)	36(3)	30(3)	-4(2)	4(3)	1(3)
C9	4095(7)	5212(7)	1747(3)	40(3)	39(3)	47(4)	-1(3)	-4(3)	0(3)
C10	4697(7)	6728(8)	1923(4)	44(4)	47(4)	55(4)	-3(3)	-4(3)	-13(3)
C11	3846(8)	8082(7)	1682(4)	66(4)	38(3)	56(4)	-5(3)	12(4)	-16(3)
C12	2432(8)	7913(7)	1259(4)	62(4)	28(3)	64(5)	2(3)	-1(4)	-1(3)
C13	1820(7)	6409(8)	1089(3)	49(3)	36(3)	49(3)	-0(3)	-7(3)	0(3)

^a U_{11} or U_{iso} .

carbon atoms of 2-diethylaminoethanolato ligand had unusually large thermal motion, and a difference Fourier map proved the structure to be disordered. The carbon atoms of $(C_2H_5)_2LO$ were given site

occupation factors 0.5 which were refined, but they showed no significant change and were fixed at 0.5. After some least-squares refinements the A and B forms of the 2-diethylaminoethanolato ligand were

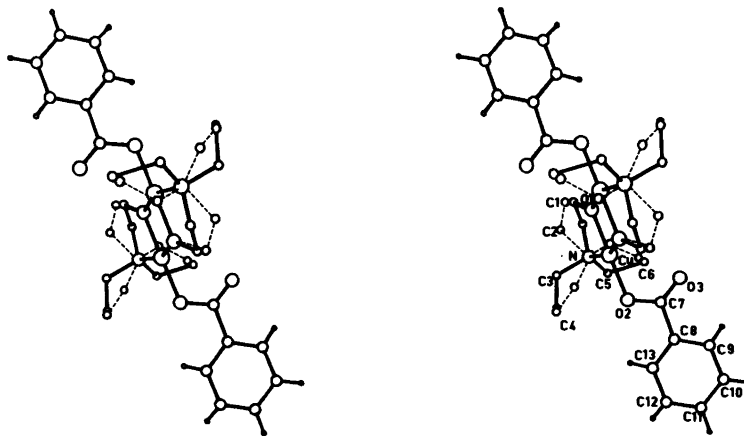


Fig. 1. Stereoview of the structure of $[Cu(C_6H_{14}NO)(C_7H_5O_2)]_2$. The A form in solid lines, the B form in dotted lines. Hydrogen atoms in the disordered part are omitted for clarity.

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters ($\times 10^2$) for hydrogen atoms.

Atom	X	Y	Z	U
H1(C1A)	-2364	-1120	915	48
H2(C1A)	-2302	-2645	440	48
H1(C1B)	-3094	-1841	-105	59
H2(C1B)	-3155	-315	370	59
H1(C2A)	-1426	-32	1344	109
H2(C2A)	-2742	-1230	1472	109
H1(C2B)	-4244	-170	743	104
H2(C2B)	-2953	1085	643	104
H1(C3A)	-2697	1411	526	102
H2(C3A)	-4376	1738	679	102
H1(C3B)	-3444	2743	1612	123
H2(C3B)	-1766	2380	1467	123
H1(C4A)	-3781	4559	384	87
H2(C4A)	-1990	4488	679	87
H3(C4A)	-3194	4178	1178	87
H1(C4B)	-2508	4044	266	84
H2(C4B)	-4261	3652	279	84
H3(C4B)	-2945	2578	706	84
H1(C5A)	-1209	2296	1477	112
H2(C5A)	-2174	2266	2087	112
H1(C5B)	-602	-282	1912	108
H2(C5B)	-2239	-145	2136	108
H1(C6A)	262	433	2657	99
H2(C6A)	376	2121	2300	99
H3(C6A)	872	547	1945	99
H1(C6B)	-103	372	2700	79
H2(C6B)	-981	445	1923	79
H3(C6B)	-686	2038	2366	79
H1(C9)	4570(63)	4409(71)	1949(29)	53
H1(C10)	5699(66)	6872(71)	2271(30)	59
H1(C11)	4251(65)	9051(72)	1762(30)	62
H1(C12)	1974(67)	8669(73)	1134(30)	64
H1(C13)	863(72)	6284(80)	804(31)	58

derived. The corresponding bond lengths of the A and B forms were given the same value and refined as such.

The structure was refined by the blocked-cascade full-matrix least-squares method⁴ with anisotropic temperature factors for non-hydrogen atoms except for the fractional occupancy atoms C1, C4 and C6. The hydrogen atoms were included with fixed bond lengths (C-H=0.96 Å) and constrained angles at calculated positions. The isotropic thermal parameters for the hydrogen atoms were set 1.2 times the equivalent isotropic thermal parameters for the corresponding carbon atom. Finally the positions of the hydrogen atoms in the benzoato ligand were refined.

Table 3. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

The copper(II) environment			
Cu-O1	1.902(4)	O1-Cu-N	84.7(2)
Cu-O2	1.888(4)	O1-Cu-O2	175.7(2)
Cu-N	2.042(4)	O1-Cu-O1 ⁱ	76.2(2)
Cu-O1 ⁱ	1.925(4)	N-Cu-O2	99.2(2)
Cu...O3	2.907(4)	N-Cu-O ⁱ	159.6(2)
Cu...Cu	3.011(1)	O2-Cu-O1 ⁱ	99.7(2)
		Cu-O-Cu ⁱ	103.8(2)
The 2-diethylaminoethanolato ligand			
Form A		Form B	
O1-C1	1.42(1)	O1-C1	1.42(1)
C1-C2	1.48(2)	C1-C2	1.48(2)
N-C2	1.52(1)	N-C2	1.52(2)
N-C3	1.52(2)	N-C3	1.52(2)
N-C5	1.56(1)	N-C5	1.56(2)
C3-C4	1.57(2)	C3-C4	1.57(3)
C5-C6	1.54(3)	C5-C6	1.53(2)
Cu-N-C2	102.7(9)	Cu-N-C2	106.0(9)
Cu-N-C3	108.3(8)	Cu-N-C3	119.8(9)
Cu-N-C5	111.1(7)	Cu-N-C5	115.1(8)
C2-N-C3	114.8(10)	C2-N-C3	110.6(10)
C2-N-C5	106.0(9)	C2-N-C5	95.9(11)
C3-N-C5	113.4(10)	C3-N-C5	106.9(10)
N-C2-C1	113.4(12)	N-C2-C1	114.7(9)
N-C3-C4	113.9(11)	N-C3-C4	106.7(15)
N-C5-C6	115.0(15)	N-C5-C6	108.6(13)
O-C1-C2	107.3(10)	O-C1-C2	112.3(8)
C1-O-Cu	117.9(5)	C1-O-Cu	116.5(4)
C1-O-Cu ⁱ	138.2(5)	C1-O-Cu ⁱ	132.5(4)
The benzoato ligand			
O2-C7	1.299(7)	Cu-O2-C7	116.1(3)
O3-C7	1.205(7)	O2-C7-O3	124.9(5)
C7-C8	1.518(8)	O2-C7-C8	114.2(5)
C8-C9	1.381(8)	O3-C7-C8	120.9(5)
C9-C10	1.378(9)	C7-C8-C9	119.2(5)
C10-C11	1.378(9)	C7-C8-C13	121.9(5)
C11-C12	1.364(9)	C8-C9-C10	120.7(5)
C12-C13	1.369(9)	C9-C10-C11	119.6(6)
C13-C8	1.383(8)	C10-C11-C12	119.9(6)
		C11-C12-C13	120.7(6)
		C13-C8-C9	118.8(5)
		C12-C13-C8	120.3(5)

i: -x, -y, -z

The refinement converged to a conventional *R* of 0.056 and a weighted discrepancy factor of 0.052,

$$R_w = \frac{\sum ||F_o| - |F_c|| \sqrt{w}}{\sum |F_o| \sqrt{w}}$$

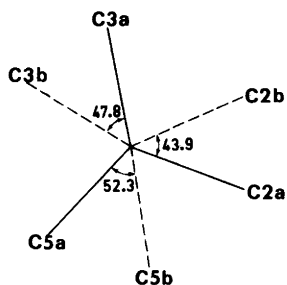


Fig. 2. Projection down the Cu–N bond with the rotation angles between the A and B positions.

with the weighing scheme $w^{-1} = \sigma^2(F_o) + 0.0005F_o^2$.

The neutral atom scattering factors have been taken from *International Tables for X-Ray Crystallography*.⁵ The calculations were performed on a Nicolet R3m diffractometer system with SHELXTL⁴ software for a minicomputer (Nova 3). The final atomic parameters are given in Tables 1 and 2, and bond distances and angles in Table 3.

DISCUSSION

In the unit cell there are two dimeric molecules, which are centrosymmetric and bridged by 2-diethylaminoethanolato oxygen atoms. In the Cu_2O_2 core the Cu...Cu distance of 3.011(1) Å is very similar to that in other dimeric alkoxy-bridged Cu(II) complexes with *N,N*-dialkylaminoethanols where the distances vary from 2.950 Å to 3.026 Å.¹ Also the Cu–O–Cu' and O–Cu–O' angles of 103.8(2) and 76.2(2)° agree well with those in other dimers.¹ The deviations from the Cu_2O_2 plane for the benzoato oxygen atom O2 and the nitrogen atom are 0.047 and 0.251 Å, respectively.

The coordination around the copper(II) ion is square-planar and the basal plane consists of two

bridging ethanolato oxygen atoms, one benzoato oxygen atom and one nitrogen atom. The bond lengths are Cu–O1 1.902(4) Å, Cu–O1' 1.925(4) Å, Cu–O2 1.888(4) Å and Cu–N 2.042(4) Å. These are quite normal distances for the coordination bonds.¹ The coordination sphere has slightly tetrahedral distortion where the O1 and O2 atoms lie 0.06 and 0.04 Å above and N and O1' 0.05 and 0.05 Å below the least-squares plane of atoms O1, O2, N, O1'. The dihedral angle between the Cu, O1, O1' and Cu, N, O2 planes is 7.5°. The distance between the copper atom and the uncoordinated benzoato oxygen atom O3 is 2.907(4) Å and the angle between the basal plane and the Cu–O3 line is 45.4°.

The structure of 2-diethylaminoethanolato ligand is disordered and there are two forms, A and B, Figs. 1 and 2. In both of them the carbon atoms have the site occupation factors of 0.5. Because some atoms of the A and B forms are quite close to each other (*e.g.* C4a–C4b 0.404 Å), the coordinates were selected such that the angles and bond lengths would be as reasonable as possible. Rotation (av. 48.0°) around the Cu–N bond changes the form from A into B. The rotation angles between the A and B form for atoms C2, C3 and C5 are 43.9 and 52.3°, respectively, (Fig. 2). The dihedral angle NCIC20 in the five-membered ring is 38.4 and 9.3° in A and B, respectively. Similar disorder has been reported in the $[\text{Cu}(\text{C}_6\text{H}_{14}\text{NO})\text{NCS}]_2$ ⁶ complex, where one ethyl group and one ring carbon atom have the occupancy factors 0.5. The rotation angles around Cu–N bond were 45.4° (C ring) and 47.5° (C ethyl).

The benzoato ligand is almost planar, the oxygen atom O2 having (0.008 Å) the largest deviation from the least-squares plane. The dihedral angle between the phenyl ring plane and its carboxyl group is 5.4° and between the phenyl ring and the Cu_2O_2 plane 78.1°. The mean value of the ring C–C bond and C–C–C angle are 1.375 Å and

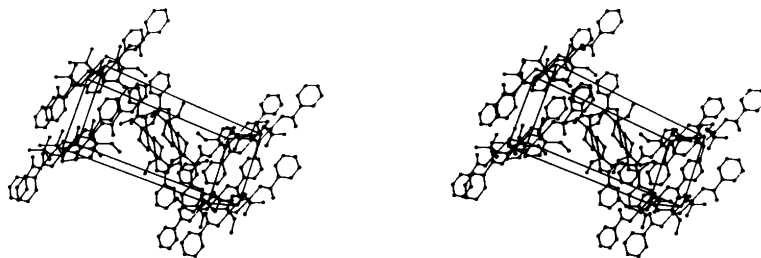


Fig. 3. Stereoview of the packing. The B form is omitted for clarity.

120.0°. The benzoato ligand is unidentate with the C7–O2–Cu angle of 116.1(3)°. The bond lengths and angles agree well with other data reported.^{2,7–10} The coordinated C–O bond length is 0.09 Å longer than the uncoordinated one which has more double-bond character. The C–H bond lengths in the phenyl ring vary from 0.76 to 1.01 Å with a mean value of 0.88 Å.

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